



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 14/26, 14/18, 16/24	A1	(11) International Publication Number: WO 90/14368 (43) International Publication Date: 29 November 1990 (29.11.90)
(21) International Application Number: PCT/US90/02604 (22) International Filing Date: 14 May 1990 (14.05.90) (30) Priority data: 354,194 19 May 1989 (19.05.89) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: LOGOTHETIS, Anestis, Leonidas ; 2816 Kennedy Road, Wilmington, DE 19810 (US). (74) Agents: HUNTLEY, Donald, W. et al.; E.I. du Pont de Nemours and Company, Legal Department, 1007 Market Street, Wilmington, DE 19898 (DE).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: PREPARATION OF CYANO-CONTAINING PERFLUOROPOLYMERS HAVING IODINE CURESITES (57) Abstract In the preparation of perfluoropolymers by the interpolymersization of tetrafluoroethylene, perfluoro (alkyl vinyl) ether and cyano-cure site monomer, the improvement of incorporating iodo moieties by the reaction of iodo-compounds of the formula RI_n , in which R is a hydrocarbon or halocarbon radical of 1 to 8 carbon atoms and n is 1 or 2.		

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TITLEPREPARATION OF CYANO-CONTAINING
PERFLUOROPOLYMERS HAVING
5 IODINE CURESITESBACKGROUND OF THE INVENTION

Perfluoroelastomers have long been used in a variety of applications that require excellent
10 resistance to high temperature and chemical attack. One particularly outstanding fluoropolymer that has been used in elastomeric applications is that prepared from tetrafluoroethylene (TFE) and perfluoro (alkyl vinyl) ether, and particularly perfluoro (methyl vinyl)
15 ether (PMVE). To facilitate the crosslinking in these copolymers that is essential to good elastomeric properties, a small percentage of termonomer is generally incorporated, such as the cyano-containing fluoroolefins described in Breazeale, U.S. Patent
20 4,281,092.

While these cyano-perfluoroelastomers have exhibited outstanding thermal and oxidative stability, continuing effort has been directed to further
modification of these polymers to broaden the areas in
25 which they can be used. Particular attention has been paid to the rate and thoroughness of the curing reaction that has been used with perfluoroelastomers. Specifically, the perfluoropolymers previously made from TFE, PMVE and a cure site monomer typically
30 exhibit a high concentration of ionic end groups, such as carboxylic or sulfonic acid moieties, which are introduced from the initiating system. Conventional chain transfer agents can be used to lower the concentration of the ionic end groups and also lower
35 the polymer viscosity. However, the physical

properties of these polymers are generally depreciated with such chain transfer agents.

SUMMARY OF THE INVENTION

5 The instant invention relates to improved perfluoropolymer compositions which, when compounded and cured as elastomers, exhibit an excellent combination of curing and mold release characteristics.

Specifically, the present invention provides, in a process for the preparation of perfluoropolymer by
10 the random copolymerization of tetrafluoroethylene, perfluoro (alkyl vinyl) ether and fluorinated curesite monomer containing nitrile groups, the improvement wherein the copolymerization reactants further comprise compounds of the formula RI_n , in which R is a
15 hydrocarbon or halocarbon radical of 1 to 8 carbon atoms and n is 1 or 2.

DETAILED DESCRIPTION OF THE INVENTION

The basic components of the present perfluoropolymers, the tetrafluoroethylene and the
20 perfluoro (alkyl vinyl) ether, and their polymerization, are described in Harris et al, U.S. Patent 3,132,123, which is hereby incorporated by reference. Of the perfluoro (alkyl vinyl) ethers, perfluoro (methyl vinyl) ether (PMVE) has been found to
25 be particularly satisfactory. Other perfluoro (alkyl vinyl) ethers which can be used in the present invention include perfluoro (alkoxy alkyl vinyl) ethers, such as those described in Fritz et al., U.S. Patent 3,291,843, also hereby incorporated by
30 reference. Of those perfluoro (alkoxy alkyl vinyl) ethers, perfluoro (5-methyl-3,6-dioxa-1-nonene) has been found to be particularly satisfactory.

A wide variety of cyano- cure sites can be incorporated into these polymers, including those
35 described in Breazeale, U.S. Patent 4,281,092, hereby

incorporated by reference. The polymers resulting from this invention preferably contain such curesites randomly distributed along the backbone of the perfluoropolymer.

5 A central aspect of the present invention is that the perfluoropolymer comprise iodine moieties. The iodo moieties can be incorporated by conducting the radical copolymerization of the basic monomers noted above in the presence of an iodine-containing compound
10 represented by the formula RI_x , where R is a hydrocarbon or saturated fluorocarbon or chlorofluorocarbon residue having 1 to 8 carbon atoms and x is an integer of 1 or 2, corresponding to the valence of the residue R.

15 In the course of the radically initiated copolymerization, the iodo compound acts as a chain transfer agent, resulting in a telomerization polymerization process in which a labile, iodine-containing chain end is formed, and the haloalkyl
20 residue of the iodo compound is attached to the other end of the polymer chain. If the iodo compound has two iodo groups, the fluoropolymer chain may therefore have iodine groups at each end, and the telomerization polymerization process will occur at each end of the
25 polymer chain.

 Iodo-compounds which can be used in the preparation of the perfluoropolymers according to the present invention include, for example, those based on hydrocarbon residue such as methylene iodide,
30 1,4-diiodo butane, and butyl iodide, and those based on saturated fluorocarbon or chlorofluorocarbon residue such as monoiodo perfluoromethane, diiodo methane, monoiodo perfluoroethane, monoiodo perfluoro propane, monoiodopropane, 1,3-diiodoperfluoro-n-propane, 1,4-
35 diiodo-n-butane, 1,4-diiodoperfluoro-n-butane,

1,3-diiodo-2-chloroperfluoro-n-propane and
1,5-diiodo-2,4-dichloro-perfluoro-n-pentane. Other
iodo-compounds which can be used include those
described in U.S. Patent 4,243,770, hereby incorporated
5 by reference.

The amount of iodo-compound used should be
high enough to give extensive chain transfer and result
in incorporation of at least about 0.05 weight % of
iodine in the perfluoropolymer. High chain transfer
10 efficiency by the alkyl iodide results in a
perfluoropolymer with lower compound viscosity and a
relatively narrow molecular weight distribution with a
typical value of M_w/M_n of about 2-3, for desirable
rheology and processing characteristics.

15 In general, the concentration of iodine in
the polymer should be about from 0.05 to 1.0 weight %,
and preferably 0.1-0.5 weight %, based on the
perfluoropolymer composition. The concentration in the
fluoropolymer will depend upon the concentration of
20 alkyl iodides in the polymerization medium and upon
polymerization conditions, which will effect the chain
transfer efficiency. The upper limit on iodine content
corresponds approximately to the practical lower limit
on polymer viscosity, since higher concentrations of
25 iodine gives polymers with lower molecular weight and
viscosity. The iodine concentration in the
perfluoropolymer can be determined by conventional
analytical techniques, such as elemental analysis.

The lower limit of iodine incorporation is
30 approximately that at which a significant effect on the
cure rate and vulcanizate properties is found when
cured by peroxides. The upper limit on iodine content
corresponds approximately to the practical lower limit
on polymer viscosity, since higher concentrations of
35 iodine gives polymers with lower molecular weight and

viscosity. The upper limit on iodine content also relates to the desired highest state of cure, insofar as it relates to the efficiency of formation of chains terminated with iodo groups.

5 The components of the perfluoropolymers are present in the amounts generally used in the preparation of copolymers of tetrafluoroethylene, perfluoro (alkyl vinyl) ether and cure site monomer, as described, for example, in the aforementioned U.S. Patent 4,281,092. Concentrations of about from 0.1 to 10 5.0 weight % of the cyano- moiety have been found to provide particularly good processing characteristics.

 According to the present invention, the perfluoropolymers are made by free radical emulsion 15 polymerization in a continuous stirred tank reactor, as described, for example, in the aforementioned U.S. Patent 4,281,092, and under the general reaction conditions used in the past for the preparation of perfluoropolymers. Specifically, polymerization 20 temperatures can be in the range of about from 40 to 130°C, and preferably about from 70 to 115°C, at pressures of about from 2 to 8 MPa and residence time 10 to 240 minutes. Free radical generation is effected using a water-soluble initiator such as ammonium 25 persulfate, either by thermal decomposition or by reaction with a reducing agent such as sodium sulfite. The alkyl iodides can be fed into the reactor directly or as a solution. Initiator levels are set low enough so that iodine end groups predominate over those from 30 initiator fragments. This leads to the desired low polymer viscosity and high solubility. The polymer dispersion is stabilized with an inert surface-active agent such as ammonium perfluorooctanoate, usually with addition of a base such as sodium hydroxide or a buffer

such as disodium phosphate to control pH in the range 3 to 7.

After polymerization, unreacted monomer is removed from the reactor effluent latex by vaporization at reduced pressure. Polymer can be recovered from latex by coagulation, e.g., by reducing pH to about 3 by acid addition and adding a salt solution such as calcium nitrate, magnesium sulfate, or potassium aluminum sulfate in water, followed by separation of serum from polymer, washing with water, and drying of the wet polymer. The iodine concentration in the perfluoropolymer can be determined by conventional analytical techniques, such as elemental analysis.

Perfluoropolymers made according to the present invention are typically compounded with one or more of the additives known to be useful in perfluoropolymer compositions, such as pigments, fillers, pore-forming agents and plasticizers. It is particularly advantageous to add carbon black to the fluoroelastomer to increase its modulus. Usually amounts of from 5-50 parts per hundred parts of fluoroelastomer are used, with the particular amount determined from the particle size of the carbon black and the desired hardness and modulus of the cured composition.

The compounds are generally cured by a free radical process. A curable composition comprises polymer and a peroxide to generate free radicals at curing temperatures. A dialkyl peroxide which decomposes at a temperature above 50°C is especially preferred when the composition is to be processed at elevated temperatures before it is cured. A di-tertiarybutyl peroxide having a tertiary carbon atom attached to peroxy oxygen may be particularly

beneficial in many cases. Among the most useful peroxides of this type are 2,5-dimethyl-2,5-di(tertiarybutylperoxy) hexyne-3 and 2,5-dimethyl-2,5-di(tertiarybutylperoxy) hexane. Other
5 peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, tertiarybutyl perbenzoate, and di[1,3-dimethyl-3-(t-butylperoxy) butyl]carbonate, and the like.

The resulting perfluoroelastomers exhibit
10 particularly good processing characteristics, including curing and mold release properties.

Perfluoroelastomers of TFE, PMVE and cure site monomer have typically been difficult to process in milling, extrusion and molding operations, because of their high
15 bulk viscosities. While the superior performance of the present compositions is not fully understood, it is believed that the selection of iodo compounds, which function as chain transfer agents, results in iodo end groups for the polymer chains, and these end groups are
20 reactive to crosslinking agents. When used in conjunction with the known cyano- cure sites, the iodides permit the curing of relatively low molecular weight polymers with peroxides to give parts with very good properties. The polymers can be cured with
25 greater ease and with high yields. In addition, complicated parts which could not be made with previously available perfluoroelastomers can be fabricated with the present perfluoroelastomers using transfer and injection molding techniques.

30 The perfluoropolymers made according to the present invention react with peroxide curing agents and crosslinking coagents to give unique polymer networks in which crosslinks are formed both at random points along the polymer chain and at the ends of the chains.
35 Such polymers have excellent strength and compression

set properties, as well as good processing characteristics.

The perfluoropolymers per se, without fillers or curing, can also be used in a wide variety of applications. In addition to the usual applications for which perfluoroelastomers have previously been found to provide particular benefits, the present compositions have been found to be particularly useful as antireflective coatings for pellicles, for example, in the protection of printed circuits. Specifically, a coating of perfluoroelastomers of the present invention of about from 0.2 to 1.0 microns, on a substrate of nitrocellulose, provides a pellicle material having an outstanding combination of adhesion to both the nitrocellulose film and to the pellicle frame as well as excellent optical transmittance.

The present invention is further illustrated by the following specific examples.

Examples 1-5 and Control Example A

In Example 2, perfluoroelastomer was prepared from TFE, PMVE, and perfluoro-(8-cyano-5-methyl-3,6-dioxa-1-octene) (8CNVE), with perfluoroalkyl iodides (RfI or IRfI), which provided iodo moieties on the ends of some of the polymer chains. This polymer had 8CNVE cure sites randomly dispersed in the backbone.

The polymers were prepared in a 1 liter mechanically agitated, waterjacketed, stainless-steel autoclave operated continuously at 90°C and 4800 KPa into which was pumped, at a rate of 250 ml/hr an aqueous polymerization medium/initiator solution comprising of 8 liters of water, 32 g. ammonium persulfate, 260 g. of disodium hydrogen phosphate heptahydrate, and 280 g. of ammonium perfluorooctanoate

("Fluorad" FC-143, 3M Co.). At the same time, a separate solution of 8CNVE in F-113 "Freon" at the rate of 5.6 ml/hr (the solution contained 3.0g of 8CNVE, the rest being F-113) and another separate solution of 3.4 ml/hr of 1,4-diiodoperfluorobutane in F-113 (0.67 g. the rest being F-113) were being pumped in. A gaseous stream of tetrafluoroethylene (70 g/hr) and perfluoro(methyl vinyl) ether (85 g/hr) was also fed simultaneously to the autoclave at a constant rate by means of a diaphragm compressor.

Polymer latex was removed by means of a let-down valve and unreacted monomers were vented. The latex from 14 hrs operations was added with stirring to a preheated (95°C) coagulating solution consisting of 1840 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 40 liters of water. The coagulated crumb was filtered off, washed repeatedly with water and dried by heating in an 80°C oven for 48 hrs in the presence of air. The dried polymer weighed 1825 gs. and had the composition, as weight % of the polymer, of tetrafluoroethylene 55.6, perfluoro(methyl vinyl) ether 42.6, 8CNVE 1.4 and iodine 0.32. The inherent viscosity of the polymer was determined at 30°C using 0.2 g. of polymer per deciliter of a solvent mixture comprising (by volume) 60 parts 2,2,3-trichloro-heptafluorobutane, 40 parts perfluoro(butyltetrahydrofuran) and 3 parts diethylene glycol dimethyl ether. The Mooney viscosity of the polymer was measured after 10 minutes as 42 at 100°C and 12 at 121°C. The resulting polymer was mixed on a 2-roll rubber mill with (phr) 15 MT black, 3 triallyl isocyanurate, and 5 Luperco 101XL (Lubrizol Co) peroxide, and shaped and cured at 177°C and postcured at 232°C unrestrained under nitrogen for 26 hrs. The results are shown in Table 1.

In the remaining Examples, the above general procedure was repeated. In Control Example A, in which no iodine was incorporated, the cure rate was slowest, and the vulcanizate properties were inferior to those of Examples 1-5. The operating conditions for these Examples are summarized below.

Example	<u>A</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
TFE g/hr	70	70	70	70	70	70
10 PMVE g/hr	74	85	85	85	85	85
8CNVE g/hr	4.8	0	3.0	1.6	2.0	2.4
I(CF ₂) ₄ I g/hr	0	1.1	0.67	0.64	0.64	0.64
APS g/hr	1.0	0.4	0.4	0.4	0.4	0.4
Phosphate g/hr	3.5	3.2	3.2	3.2	3.2	3.2
15 FC-143 g/hr	4.5	4.0	4.0	4.0	4.0	4.0
Temp. °C	80	90	90	90	90	90

The resulting polymers were compounded, cured and tested as before, and the results are shown in Table 1.

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TABLE 1

IODOMODIFIED (ICF₂)₄I 8CNVE CONTAINING TFE/PMVE POLYMERS

Examples	<u>Control A</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
5	<u>Raw Polymer Description</u>					
	TFE wt %	54.9	56.3	55.6	56.1	55.2
	PMVE wt %	42.7	43.3	42.6	42.9	43.5
	8CNVE wt %	2.4	-	1.4	0.8	1.1
	8CNVE mol/kg	0.062	-	0.036	0.021	0.028
10	I wt %	-	0.40	0.32	0.24	0.29
	I mol/kg	-	0.033	0.025	0.019	0.019
	Inh. Viscosity	0.46	0.30	0.32	0.35	0.33
	Mooney at 100°C	-	35	42	65	26
	121°C	56	10	12	27	13
15	<u>Cured Properties</u>					
	ODR 177°C					
	Minimum - N.m	0.65	0.2	0.15	0.35	0.2
	mH - N.m	2.6	4.0	4.3	3.7	3.9
	ts2 - Mins	1.5	0.9	0.9	0.9	1.1
20	TC90 - Mins	7.5	1.3	2.5	2	3.2
	<u>Tensiles</u>					
	M100	510	1247	1552	1603	1273
	Tb	1386	1953	1834	1838	2092
	Eb	200	149	114	157	162
25	<u>Hardness shore A</u>	71	80	80	79	76
	<u>Comp. Set Resistance 200°C/70 hrs</u>					
	Pellets	35	41	41	55	39
	O-ring	35	55	46	58	39

- 30**
1. The compounds contained 100 parts rubber, 15 parts MT black, 3 parts of triallylisocyanurate 5 parts Luperc 101XL peroxide.
 2. The samples were press-cured at 177°C/15 mins and post-cured at 232°C for 26 hours.

Examples 6-8 and Control Example B

In Examples 6-8, TFE/PMVE/8CNVE perfluoroelastomers were prepared with hydrocarbon alkyl iodides (RI or IRI), which provided iodo moieties on the ends of some of the polymer chains. The 8CNVE cure sites in these polymers were randomly dispersed in the backbone.

The polymerization conditions were identical to those of Examples 1-5, except as reported below:

Example	<u>Control</u>	<u>6</u>	<u>7</u>	<u>8</u>
TFE g/hr	70	60	60	60
PMVE g/hr	74	75	75	75
8CNVE g/hr	4.8	3.2	3.2	3.2
ICH ₂ I g/hr	0	0.12	0.10	0.83
Phosphate g/hr	3.5	4.0	4.0	4.0
FC-143	4.5	3.6	3.6	3.6
Temp. °C	80	90	90	90

The methylene iodide was dissolved in t-butanol as a 10% solution because it was not soluble in F113. The compounding and curing were identical to the conditions used in Examples 1-5, and the results are shown in Table 2. The iodo-containing polymers of the present invention exhibit faster cure rates than the Control Example and improved vulcanizate properties.

TABLE 2

IODOMODIFIED (CH₂I₂) 8CNVE CONTAINING TFE/PMVE POLYMERS

Examples	Control B	6	7	8
<u>Raw Polymer Description</u>				
5				
TFE wt %	54.9	58.3	56.7	57.6
PMVE wt %	42.7	40	41.5	40.5
8CNVE wt %	2.6	1.6	1.7	1.8
8CNVE mol/kg	0.062	0.041	0.044	0.046
I wt %	-	0.08	0.08	0.10
10				
I mol/kg	-	0.006	0.006	0.008
Inh. Viscosity	0.46	0.45	0.45	0.42
Mooney at 100°C	-	110	104	116
121°C	56	57	52	50
<u>Cured Properties</u>				
15				
ODR 177°C				
Minimum - N.m	0.65	0.95	0.80	0.90
mH - N.m	2.60	3.80	3.90	3.95
ts2 - Mins	1.5	1.0	1.0	1.1
TC90 - Mins	7.5	3.5	3.1	2.6
20				
<u>Tensiles</u>				
M100	510	1213	1191	1196
Tb	1386	2181	2215	2104
Eb	200	156	167	154
<u>Hardness shore A</u>	71	75	74	76
25				
<u>Comp. Set Resistance 200°C/70 hrs</u>				
<u>Pellets</u>	35	43	41	44
O-ring	35	28	27	35

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- 30
1. The compounds contained 100 parts rubber, 15 parts MT black, 3 parts of triallylisocyanurate
5 parts Luperco 101XL peroxide.
 2. The samples were press cured at 177°C/15 mins and post-cured at 288°C for 46 hours.

I CLAIM:

1. In a process for the preparation of
5 perfluoropolymer by the random copolymerization of
tetrafluoroethylene, perfluoro (alkyl vinyl) ether and
fluorinated curesite monomer containing nitrile groups,
the improvement wherein the copolymerization reactants
further comprise iodo-compounds of the formula RI_n , in
10 which R is a hydrocarbon or halocarbon radical of 1 to
8 carbon atoms and n is 1 or 2.
2. A process of Claim 1 wherein the R group
in the iodo-compound is a hydrocarbon radical.
15
3. A process of Claim 1 wherein the R group
in the iodo-reactant is a halocarbon radical.
4. A process of Claim 1 wherein the iodo-
20 compound is a di-iodo compound.
5. A process of Claim 4 wherein the
iodo-compound consists essentially of
diiodoperfluorobutane.
25
6. A process of Claim 4 wherein the
iodo-compound consists essentially of
diiodoperfluorohexane.
7. A process of Claim 2 wherein the
30 iodo-compound consists essentially of methylene iodide.
8. A process of Claim 1 wherein the
perfluoro (alkyl vinyl) ether consists essentially of
35 perfluoro (methyl vinyl) ether.

9. . A process of Claim 1 wherein the perfluoro (alkyl vinyl) ether is a perfluoro (alkoxy alkyl vinyl) ether.

5 10. A process of Claim 9 wherein the perfluoro (alkoxy alkyl vinyl) ether consists essentially of perfluoro (5-methyl-3,6-dioxa-1-nonene).

10 11. A process of Claim 1 wherein the nitrile curesites comprise at least about 0.1% by weight of the perfluoropolymer, and are randomly distributed along the backbone of the perfluoropolymer.

15 12. A process of Claim 1 wherein the interpolymerization is carried out in a continuous stirred tank reactor.

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INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US90/02604**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL (5) CO8F 14/26; CO8F 14/18; CO8F 16/24 U.S. CL: 526/206, 247, 254																																			
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Classification System</td> <td style="width: 50%; border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; padding-top: 10px;">U.S.</td> <td style="border: none; padding-top: 10px;">526/206, 247, 254</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵</div>			Classification System	Classification Symbols	U.S.	526/206, 247, 254																													
Classification System	Classification Symbols																																		
U.S.	526/206, 247, 254																																		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category [*]</th> <th style="width: 60%;">Citation of Document, ¹⁰ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 30%;">Relevant to Claim No. ¹⁸</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">X Y</td> <td>EP, A, 0,153,848, 04 September 1985 (ALBIN) SEE ENTIRE DOCUMENT.</td> <td style="text-align: center;">1-12 1-12</td> </tr> <tr> <td style="text-align: center;">X Y</td> <td>US, A, 4,564,662, 14 January 1986 (ALBIN) SEE ENTIRE DOCUMENT.</td> <td style="text-align: center;">1-12 1-12</td> </tr> <tr> <td style="text-align: center;">X Y</td> <td>US, A, 4,612,357, 16 September 1986 (BEKIARIAN) SEE ENTIRE DOCUMENT.</td> <td style="text-align: center;">1-12 1-12</td> </tr> <tr> <td style="text-align: center;">A</td> <td>EP, A, 0,028,314, 14 January 1987 (OJAKAAR ET AL.)</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 3,351,619, 07 November 1967 (WARNELL)</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 4,243,770, 06 January 1981 (TATEMOTO ET AL.)</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 4,281,092, 28 July 1981 (BREAZEALE)</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 4,413,094, 01 November 1983 (AUFDERMARSH, JR)</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 4,487,903, 11 December 1984 (TATEMOTO ET AL.)</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 4,529,784, 16 July 1985 (FINLAY)</td> <td style="text-align: center;">1-12</td> </tr> </tbody> </table>			Category [*]	Citation of Document, ¹⁰ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸	X Y	EP, A, 0,153,848, 04 September 1985 (ALBIN) SEE ENTIRE DOCUMENT.	1-12 1-12	X Y	US, A, 4,564,662, 14 January 1986 (ALBIN) SEE ENTIRE DOCUMENT.	1-12 1-12	X Y	US, A, 4,612,357, 16 September 1986 (BEKIARIAN) SEE ENTIRE DOCUMENT.	1-12 1-12	A	EP, A, 0,028,314, 14 January 1987 (OJAKAAR ET AL.)	1-12	A	US, A, 3,351,619, 07 November 1967 (WARNELL)	1-12	A	US, A, 4,243,770, 06 January 1981 (TATEMOTO ET AL.)	1-12	A	US, A, 4,281,092, 28 July 1981 (BREAZEALE)	1-12	A	US, A, 4,413,094, 01 November 1983 (AUFDERMARSH, JR)	1-12	A	US, A, 4,487,903, 11 December 1984 (TATEMOTO ET AL.)	1-12	A	US, A, 4,529,784, 16 July 1985 (FINLAY)	1-12
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																																			
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